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# Efficient xerographic photoreceptors from conjugated polymers and polymer blends

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## ABSTRACT

Bilayer xerographic photoreceptors in which  $\pi$ -conjugated polymers and binary conjugated polymer blends are used as the charge generation layer have been fabricated, evaluated, and shown to be highly efficient. Devices incorporating poly(1,4-phenylene benzobisthiazole), poly(2,5-pyridylene benzobisthiazole), poly(1,4-phenylenebisvinylene benzobisthiazole), poly(1,4-(2-hydroxy)phenylene benzobisthiazole), and poly(benzimidazobenzophenanthroline ladder) as the charge generation layer and a layer of tris(*p*-tolyl)amine (TTA) dispersed in polycarbonate as the charge-transport layer showed good photosensitivities (6–18 ergs/cm<sup>2</sup>), good dark decay characteristics (2–10 V/s at surface potentials of 400–600 V), and high charge generation quantum efficiencies (20–50% at  $\sim 10^6$  V/cm). Photoreceptors using binary blends of conjugated polymers had enhanced spectral range of photosensitivity (300–700 nm) and significantly enhanced quantum yield for charge photogeneration relative to the component conjugated polymers. Photocarrier generation in these bilayer photoreceptors is *extrinsic* in nature and is mediated by exciplex formation between the conjugated polymer and TTA at the bilayer interface. Observed nanoscale size effects, in which the photoreceptor performance (quantum efficiency, photosensitivity) is enhanced with decreasing size of the charge generation layer, provide a means of tuning the photoconductive properties of optoelectronic devices based on conjugated polymers. A model derived from Onsager's 1934 theory was used to estimate the primary quantum yield of ion-pairs and ion-pair separation distance in the bilayer photoreceptors to be 0.21–0.62, and 4–6 Å, respectively.

**Keywords:** photoreceptors; conjugated polymers; polymer blends; charge photogeneration; nanoscale size effects.

## INTRODUCTION

Organic photoconductive materials are currently used as photoreceptors in electrographic imaging systems such as photocopiers, laser printers, and fax machines.<sup>1,2</sup> Such organic photoreceptors are typically bilayer devices in which one layer serves as the charge generation layer (CGL) and the other layer serves as the charge transport layer (CTL). Current CTL materials are typically triarylamine molecules dispersed in an inert polymer matrix.<sup>1,3,4</sup> Since the development of hole-transport materials is more advanced than that of electron-transport materials, current commercial organic photoreceptors are fabricated with CTL materials that transport holes.<sup>1,5</sup> Current organic CGL materials include metallophthalocyanines, perylene pigments, squaraines, and azo compounds dispersed in polymer matrices.<sup>2</sup> Such dye molecule-doped polymer systems are in general metastable materials that are subject to phase separation and crystallization over time, reducing the long-term stability and performance of photoreceptors. We recently explored  $\pi$ -conjugated polymers as *single-component* CGL materials in xerographic photoreceptors.<sup>6–9</sup> Conjugated polymers have also been shown to be promising materials for other optoelectronic applications such as photodiodes, photovoltaic cells, and light-emitting diodes.<sup>10</sup> Key to many of these applications are the processes of generation, injection, transport, and recombination of charge carriers in the materials. This paper focuses on the photoconductive properties, particularly charge photogeneration phenomena, in  $\pi$ -conjugated polymers

in the context of developing the materials for electrophotographic imaging and other optoelectronic applications.

Intrinsic photoconductivity of conjugated polymers has been previously studied in polyacetylene,<sup>11</sup> polydiacetylenes,<sup>12</sup> poly(phenylene vinylenes),<sup>13</sup> poly(3-alkylthiophenes),<sup>14</sup> and polyquinolines.<sup>15</sup> Extrinsic photoconductivity of conjugated polymers has also been reported in polymer-C<sub>60</sub> heterojunctions,<sup>10(a)</sup> polymer-C<sub>60</sub> composites,<sup>16</sup> polymer-polymer blends,<sup>17</sup> and bilayer assemblies of n-type conjugated polymers with triaryl amines.<sup>6-9</sup> It was found that in these conjugated polymer systems, photoinduced electron transfer played a critical role in the enhancement of extrinsic photoconductivity compared to the intrinsic photoconductivity of the pure polymers. For example, enhanced charge photogeneration in bilayer photoreceptors using conjugated polymers was previously reported by our laboratory.<sup>6-9</sup> In such bilayer photoreceptor devices, conjugated polymers were used as the charge-generation layer (CGL) and a molecularly-doped-polymer TTA:PC [tris(*p*-tolyl)amine):polycarbonate] was employed as the charge-transport layer (CTL). The TTA:PC system has been shown to be a trap-free hole transporting material.<sup>3</sup> A variety of experimental measurements including photogeneration quantum efficiency as a function of electric field, picosecond photoinduced absorption, and steady-state and time-resolved photoluminescence spectroscopy on the bilayer devices suggested that exciplex formation between the n-type conjugated polymer (acceptor) and TTA (donor) plays a critical role in the process of charge photogeneration.<sup>6-9</sup>

In this paper, we report the fabrication and evaluation of bilayer photoreceptors using n-type (electron transporting) conjugated polymers, such as poly(1,4-phenylene benzobisthiazole) (PBZT), poly(1,4-phenylenebisvinylene benzobisthiazole) (PBTPV), poly(2,5-pyridylene benzobisthiazole) (PPyBT), poly(1,4-(2-hydroxy)phenylene benzobisthiazole) (HPBT), and poly(benzimidazobenzophenanthroline ladder) (BBL) as the charge generation layer and tris(*p*-tolyl)amine doped polycarbonate (TTA:PC) as the charge transport layer. Quantum efficiency of charge photogeneration in these photoreceptors was measured at electric fields of 10<sup>4</sup>–10<sup>6</sup> V/cm by applying the xerographic photodischarge technique. It is shown that the performance of the conjugated polymer-based bilayer devices (dark decay, photosensitivity, and quantum efficiency) is comparable to commercial organic photoreceptors.<sup>1,2</sup> The primary quantum yield of ion-pairs  $\phi_0$  and the ion-pair separation distance  $r_0$  in the new photoreceptors were obtained from the measured electric field dependent charge photogeneration efficiency by a theoretical model<sup>24</sup> developed with the aid of Onsager's 1934 theory.<sup>25</sup> Nanoscale size effects on photogeneration in bilayer photoreceptors was also explored by varying the thickness of the conjugated polymer CGL. Finally, we report on initial studies aimed at the enhancement of photogeneration quantum efficiency and the spectral range of photosensitivity in bilayer photoreceptors by using conjugated polymer blends as the CGL.

## EXPERIMENTAL SECTION

**Materials.** The molecular structures of the conjugated polymers, TTA, and polycarbonate used to fabricate xerographic photoreceptors are shown in Figure 1. The synthesis and detailed characterization of the conjugated polymers used in our studies have been reported elsewhere: PBZT,<sup>20(a),20(b)</sup> PBTPV,<sup>20(b),20(c)</sup> PPyBT,<sup>20(d),20(e)</sup> HPBT,<sup>20(f)</sup> BBL.<sup>20(g)</sup> Polycarbonate and TTA were provided by Eastman Kodak company and used without further purification.

**Device Fabrication.** Bilayer photoreceptors consisting of a thin layer (9–195 nm) of a conjugated polymer and a thick layer (10–22  $\mu$ m) of a trap-free tris(*p*-tolyl)amine (TTA) doped polycarbonate (TTA:PC) were used in our studies. The bilayer devices were fabricated on a Ni-coated poly(ethylene terephthalate) (PET) substrate (Figure 2). The molecularly-doped polymer system TTA:PC is known to be a trap-free material,<sup>3</sup> which means that charges photogenerated or injected into it can move through it over long distances without being trapped. In the case of TTA-doped polycarbonate used here, it is a trap-free *hole* transport material.<sup>3</sup>

The Lewis acid coordination complexation method<sup>21</sup> was used to prepare isotropic solution of each conjugated polymer or polymer blend in nitromethane containing aluminum chloride (AlCl<sub>3</sub>) or gallium chloride (GaCl<sub>3</sub>). Bilayer devices on which photodischarge measurements were performed were prepared by spin coating a solution of the conjugated polymer onto nickel-coated PET substrates. The pure polymer

films were obtained by regeneration of the polymer-Lewis acid complex in deionized water.<sup>21</sup> The polymer films obtained were vacuum dried at 80 °C overnight and were subsequently overcoated with a TTA:PC layer. The TTA:PC layer was in the ratio of 40:60 by weight and was blade coated from a dichloromethane solution and dried in vacuum at 40 °C overnight. The films for the absorption measurement were prepared on silica substrates by following the same procedures described above. Polymer film thicknesses were measured by using a profilometer (Tencor Instruments, Model 200 Alpha-step) and by an optical technique based on the known absorption coefficients of the polymers.

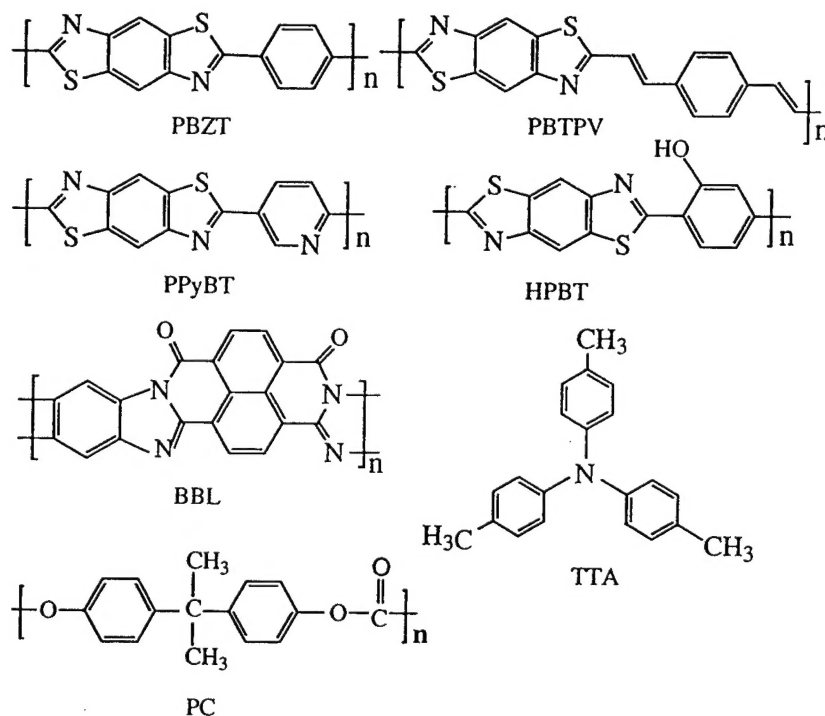


Figure 1. Chemical structures of the materials used in this study.

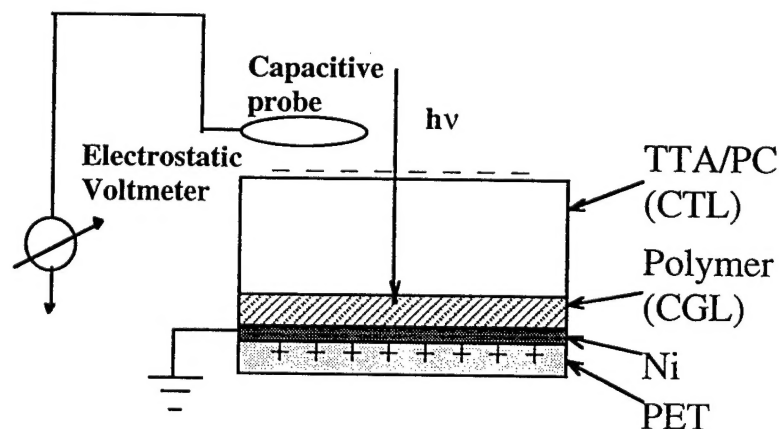


Figure 2. Schematic of a conjugated polymer photoreceptor.

**Evaluation of Devices.** Optical absorption spectra were obtained with a Perkin Elmer Model Lambda 9 UV-vis-near IR spectrophotometer. Details of the xerographic photodischarge equipment and its use for measurement of charge photogeneration were described previously.<sup>7</sup> The bilayer device shown in Figure 2 was mounted in a xerographic cycling chamber designed so that either a corona charger or a Monroe Electronics Model 114S-4 electrostatic voltmeter detector can be positioned in front of the sample. The device was charged to the desired surface potential (negative) with a corona charger supplied by a Universal Voltronics high-voltage source. An electrostatic voltage detector placed in front of the device measured the surface potential. A photoreceptor device under test was illuminated by a 45-watt tungsten lamp passing through a Bausch and Lomb monochromator. The intensity of the exposing radiation was kept low (2~2.5 ergs/cm<sup>2</sup>) to minimize space charge effects. The resulting photodischarge data were acquired using a computer program. The quantum efficiency for charge photogeneration was determined from the initial rate of discharge of the device.<sup>22</sup>

$$\phi = \frac{\epsilon\epsilon_0}{elI} \left( \frac{dV}{dt} \right)_{t=0} \quad (1)$$

where  $\epsilon$  is the dielectric constant,  $\epsilon_0$  the permittivity of free space,  $e$  the electronic charge,  $l$  the bilayer film thickness,  $I$  the light intensity absorbed,  $V$  the surface potential, and  $t$  the time. The field across the device was taken as  $V/l$ , and the exposure time was set to be 1.2 s. The bilayer film thickness for all the photoreceptors investigated was in the range of 10 to 22  $\mu\text{m}$ . All measurements were made at room temperature ( $\sim 22^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

**Optical Absorption Spectra.** Figure 3 shows the optical absorption spectra of single-layer thin films of PBZT, PBTPV, PPyBT, HPBT, and BBL on silica substrates. The strong absorption bands of these conjugated polymers in the visible range meet the spectral requirement for photoreceptors in copier applications.<sup>2</sup> The optical absorption lineshapes of PBZT, PBTPV, PPyBT, and HPBT are very similar because of their general structural similarity as members of conjugated polybenzobisthiazoles. However, due to the different linkages in the polymer backbone, the absorption maximum varies. PBZT and PPyBT have two absorption maxima around 440 and 470 nm in the visible. Those of HPBT are red shifted to 450 and 480 nm. The absorption maxima of PBTPV are further red shifted to 480 and 515 nm. The conjugated ladder polymer BBL has a broad visible absorption with a maximum around 565 nm. The absorption band of TTA:PC film was below 350 nm and not shown. In the photogeneration experiments, the longer wavelength absorption maximum was chosen as the illumination wavelength for each polymer CGL. Therefore, the incident light will only be absorbed by the conjugated polymer layer. We also found that the optical absorption spectrum of each conjugated polymer/TTA:PC bilayer investigated was a superposition of the absorption bands of the conjugated polymer and TTA:PC layers. No new absorption band was observed in the 200 to 3200 nm spectral range, indicating that the conjugated polymer and TTA do not form observable charge transfer complex in the ground state.

**Charge Photogeneration in Photoreceptors.** Two representative photoinduced discharge curves for HPBT/TTA:PC (80-nm HPBT, 480-nm illumination) and PPyBT/TTA (33-nm PPyBT, 470-nm illumination) bilayer devices are shown in Figure 4. The devices were charged to a surface potential of  $\sim 490$  V. Three important device parameters, i.e. photosensitivity, dark decay, and residual potential, were obtained from the discharge curves. For the PPyBT/TTA bilayer device, the photosensitivity was  $\sim 6$  ergs/cm<sup>2</sup>, the dark decay was  $\sim 5$  V/s and the residual potential was  $\sim 20$  V. The HPBT/TTA:PC device showed a photosensitivity of  $\sim 15$  ergs/cm<sup>2</sup>, a dark decay of  $\sim 10$  V/s, and a residual potential of  $\sim 20$  V. The performance of photoreceptors made from different conjugated polymers is listed in Table 1. All the devices showed a residual potential of about 20 V, dark decay of 2-10 V/s, and photosensitivity of 6-18 ergs/cm<sup>2</sup>. These device properties are comparable to those reported for current organic photoconductive materials.<sup>2</sup>

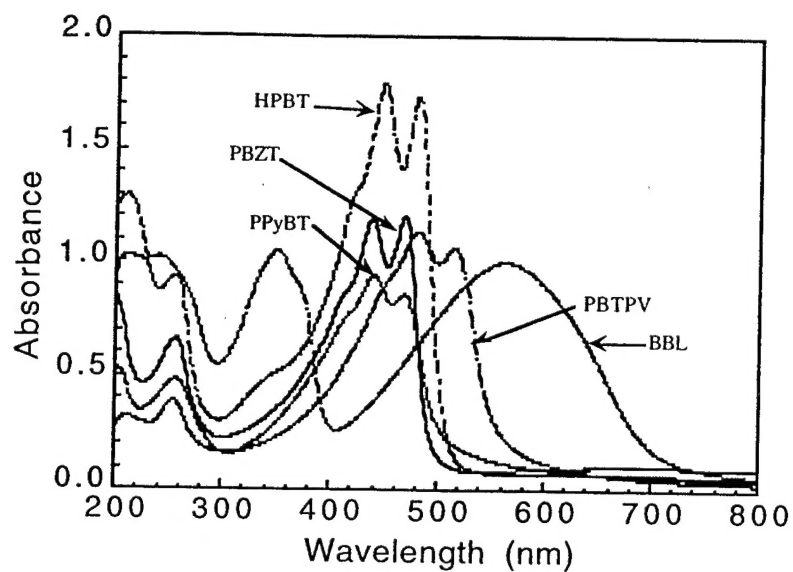


Figure 3. Optical absorption spectra of conjugated polymer thin films.

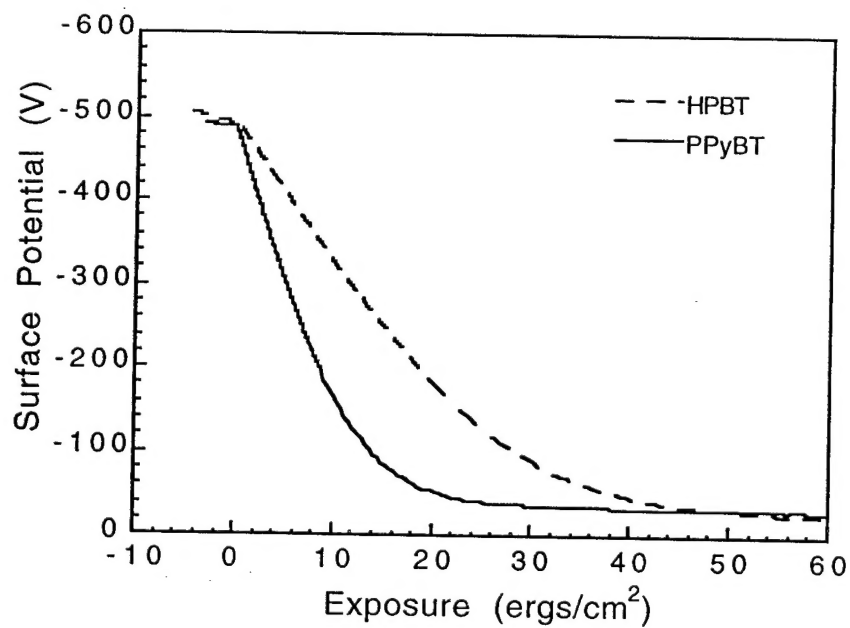


Figure 4. Photoinduced discharge curves of bilayer photoreceptors of HPBT and PPyBT.



Table 1. Photodischarge characteristics of conjugated polymer photoreceptors.

Polymer	CGL Thickness (nm)	Initial Potential (V)	Dark Decay (V/s)	Photosensitivity (ergs/cm <sup>2</sup> )	$\phi_0$	$r_0$ (Å)
PBZT	20	490	4.5	7.5	0.35	4.8
PBTPV	20	450	10.0	11.5	0.30	5.5
PPyBT	33	490	5.0	6.0	0.46	5.8
HPBT	80	490	10.0	15.0	0.24	4.1
BBL	20	480	2.0	18.0	0.32	4.6

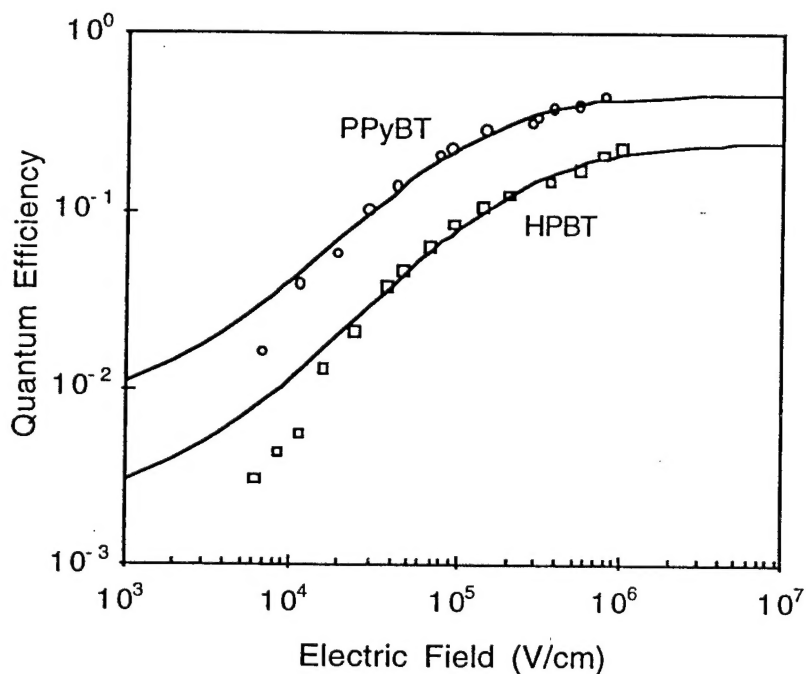


Figure 5. Charge photogeneration quantum efficiency dependence on electric field: (a) PPyBT/TTA (33-nm PPyBT, 470-nm illumination); (b) HPBT/TTA (80-nm HPBT, 480-nm illumination).

Charge photogeneration quantum efficiency of the bilayer photoreceptors were also obtained from the photodischarge measurements at electric fields of  $\sim 10^4$  to  $\sim 10^6$  V/cm. Figure 5 shows typical results for PPyBT/TTA and HPBT/TTA devices whose photoinduced discharge curves were shown in Figure 4. The quantum efficiency for photogeneration is a strong function of the electric field,  $\phi(E)$ , increasing with increasing electric field. At high electric field close to  $10^6$  V/cm, PBZT/TTA, PBTPV/TTA, PPyBT/TTA, HPBT/TTA, and BBL/TTA photoreceptors, whose photodischarge properties are listed in Table 1, had quantum efficiencies of 34%, 29%, 44%, 23%, and 21%, respectively.

The above results for the bilayer photoreceptors show that the photocarrier generation efficiency  $\phi(E)$  varies greatly with the conjugated polymer used as the CGL since the CTL material, TTA:PC was constant. Many factors, such as electronic structure and morphology of the conjugated polymer and the film



thickness of the CGL, can be expected to influence the photocarrier generation efficiency. As will be discussed later,  $\phi(E)$  can be greatly influenced by the polymer film thickness due to size effects. However, even in the case of PBZT, PBTPV, and BBL, which all have the same film thickness (20 nm, Table 1),  $\phi(E)$  varies significantly and implies that the origin of the differences in charge photogeneration must ultimately be traced to the electronic structures of the polymers. It is interesting that the 2,5-pyridylene-linked polymer, PPyBT, has by far the highest quantum yield for photogeneration at any electric field. Particularly remarkable is the large difference in  $\phi(E)$  between PPyBT and the 1,4-phenylene-linked polymer PBZT. The major difference in the electronic structures of these two benzobisthiazole polymers is that PPyBT has a higher electron affinity by  $\sim 0.2$  eV.<sup>20(d)</sup> To further elucidate the observed photocarrier generation properties of conjugated polymer-based photoreceptors we examine the interaction between the polymers and TTA at the bilayer interface.

Our laboratory has previously investigated the nature of charge photogeneration in triarylamine/conjugated polymer bilayer photoreceptor devices.<sup>6-9</sup> On the basis of several different experiments, including optical absorption spectroscopy, wavelength-dependent photogeneration quantum yield, steady-state photoluminescence, picosecond transient absorption spectroscopy, and time-resolved fluorescence measurements, it was established that the photogeneration was *extrinsic* in nature. Specifically, it was shown that charge photogeneration occurred at the TTA/conjugated polymer bilayer interface where photoinduced exciplex formation occurred and followed by field-assisted dissociation of the exciplex.<sup>6-9</sup> A schematic illustration of the exciplex model is shown in Figure 6. The conjugated polymer electron acceptor (A) when excited to its singlet excited state  $^1A^*$  may relax to the ground state either radiatively (via excimer emission<sup>8</sup>) or nonradiatively, or can form an exciplex with the electron donor (D) molecule TTA via electron transfer. The resulting exciplex ( $D-A$  or electron-hole pair) can dissociate into free charge carriers under the influence of an electric field with the rate constant  $k_d(E)$ , or deactivate to the ground state via radiative or nonradiative decay with the total rate constant  $k_f$ . The rate constant for electron and hole recombination is  $k_r$ .

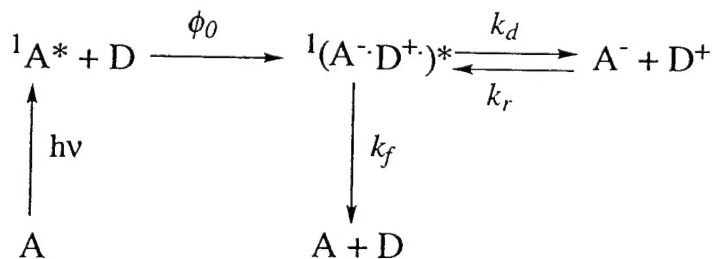


Figure 6. Schematic of exciplex-mediated charge photogeneration in conjugated polymer photoreceptors.

The exciplex-mediated charge photogeneration model can be combined with Onsager's theory to better understand the photoconductive properties of conjugated polymer photoreceptors. Electric field-dependent photogeneration quantum efficiency data for organic photoreceptors<sup>23</sup> have sometimes been analyzed by Onsager's 1938 theory.<sup>24</sup> This theory, however, predicts thermalized ion-pair separation distances of 20–30 Å. Also, the theory in most cases, does not predict the temperature dependence of the quantum efficiency  $\phi(E)$ . Theoretical kinetic models<sup>25,26</sup> derived from Onsager's 1934 theory<sup>19</sup> have been shown to give improved predictions of field and temperature dependence of quantum yield of photogeneration. We have recently developed a version of the kinetic model of charge photogeneration for application to exciplex-mediated carrier photogeneration in conjugated polymer systems where ion-pair separation distances are expected to be significantly less than 20–30 Å. In this theoretical model, the field-dependent quantum efficiency  $\phi(E)$  is written as the product of the primary ion-pair ( $D-A$  exciplex) quantum yield  $\phi_0$  which is assumed to be field-independent and the field-dependent probability for geminate ion-pair dissociation  $P(E, r_0)$ :<sup>18</sup>

$$\phi(E) = \phi_0 P(E, r_0) \quad (2)$$

where  $r_0$  is the ion-pair or donor-acceptor separation distance. The two physical parameters in equation (2) can be obtained by fitting the experimental  $\phi(E)$  data.<sup>18</sup>

The results of theoretical fit of  $\phi(E)$  data are exemplified by those for PPyBT/TTA and HPBT/TTA devices as shown in Figure 5. The solid lines in the figure represent the calculated results from the model and the two parameters  $\phi_0$  and  $r_0$ . Figure 5 shows that the experimental data and the theoretical curves are in good agreement. The ion-pair primary quantum yield  $\phi_0$  that was obtained is 0.46 for PPyBT/TTA and 0.24 for HPBT/TTA. The ion-pair separation distance  $r_0$  that best fits the data was 5.8 Å for PPyBT and 4.1 Å for HPBT/TTA. The  $\phi_0$  and  $r_0$  values for all the conjugated polymer/TTA devices are listed in Table 1. Ion-pair (donor-acceptor) separation distance of 4–6 Å obtained in the conjugated polymer/TTA bilayer systems (Table 1) is very realistic and is in the range of what can be expected for donor-acceptor separation distances in intermolecular exciplexes.<sup>27</sup> The primary ion-pair quantum yield in these bilayer photoreceptors was in the range of 0.24 to 0.46. The order of decreasing primary quantum yield  $\phi_0$  in the series of conjugated polymers in Table 1 is PPyBT > PBZT > BBL > PBTPV > HPBT. There is no obvious correlation of  $\phi_0$  with the electron affinities of the polymers,<sup>20(b)</sup> suggesting that a more detailed investigation of the ground state and excited state electronic structures of conjugated polymers will be essential to elucidate the structure- $\phi_0$  relationships.

**Nanoscale Size Effects on Photoreceptors.** We have previously reported nanoscale size effects on PPyBT/TTA bilayer photoreceptors.<sup>9</sup> A 3-fold increase in quantum efficiency of photogeneration was observed when the conjugated polymer layer (CGL) thickness was reduced from ~100 to ~10 nm. Our results showed that the primary quantum yield  $\phi_0$  of ion-pairs (D–A exciplexes) obtained from the theoretical fit of equation (2) to the experimental  $\phi(E)$  data is 0.22, 0.21, 0.45, 0.46, and 0.62 for PPyBT thickness of 195, 97, 43, 33, and 9 nm, respectively. The photosensitivity of PPyBT/TTA photoreceptors also varies with film thickness of the CGL. In contrast, the most probable ion-pair (donor-acceptor) separation distance obtained from the fit was constant at about 6 Å (5.9 Å for 9 nm, 5.8 Å for 33 nm, 5.8 Å for 43 nm, 6.0 Å for 97 nm, and 5.8 Å for 195 nm) regardless of the PPyBT film thickness. The origin of these nanoscale size effects is intimately connected with the extrinsic nature of charge photogeneration in these bilayer photoreceptors. First, the interfacial interaction (exciplex formation) between the conjugated polymer and TTA is maximized in thinner films. However, because of the small exciton diffusion length of the PPyBT only a fraction  $\phi_0$  of excitons created diffuses to the interface region and results in the formation of the ion-pair species (exciplexes). Exciton diffusion lengths of conjugated polymers are generally in the range of 5–20 nm which is much less than their absorption depths.<sup>7,28</sup> For example, the exciton diffusion length of PBZT films was 10–18 nm.<sup>7</sup> A value of about 5 nm has been reported for poly(*p*-phenylenevinylene) (PPV) films.<sup>28</sup> We expect the exciton diffusion length of PPyBT films to be about the same order of magnitude as PBZT and PPV, i.e. ~5–18 nm. Such a small exciton diffusion length in PPyBT inhibits the formation of ion-pairs (exciplexes) when the film is very thick. Thus, the closer is the conjugated polymer layer thickness to the exciton diffusion length the larger the expected  $\phi_0$ . These nanoscale size effects in conjugated polymer photoreceptors underlay the need for control of the film thickness of the CGL as well as the opportunity to enhance the performance of organic photoreceptors through nanoscale fabrication.

**Polymer Blend Photoreceptors.** Our exploration of blends of conjugated polymers as CGL materials in organic photoreceptors was motivated by the results of recent studies of the photophysical properties of binary blends of  $\pi$ -conjugated polymers in our laboratory.<sup>29–33</sup> It was found that binary blends of conjugated polymers such as those in Figure 1 were miscible over the entire composition range or phase-separated on the nanometer scale, resulting in materials with novel properties not shown by the component homopolymers.<sup>29–33</sup> Among the novel features observed in such binary blends are: spectral modulation of optical absorption with blend composition,<sup>29</sup> photoinduced electron transfer,<sup>29</sup> efficient energy transfer,<sup>30</sup> bipolar charge transport,<sup>20(f)</sup> enhanced electroluminescence,<sup>31</sup> enhanced nonlinear optical properties,<sup>32</sup> and quantum confinement effects.<sup>33</sup> The finding that the optical absorption spectra of binary blends of BBL:PBZT and BBL:HPBT were simple composition averages of those of the components<sup>29</sup> suggests that as CGL materials they could extend the spectral range of photosensitivity to 300–700 nm (see Figure 3). Similarly, observation of photoinduced electron transfer in the same binary polymer blends suggests a possible means of enhancing charge photogeneration in photoreceptors.

Figure 7 shows the optical absorption spectrum of a 80-nm thin film of a 50-mol% BBL:PBZT blend. As expected, the rather broad absorption in the range 300-700 nm is composed of the characteristic absorption bands of BBL and PBZT. The more intense absorption in the 420-480 nm spectral range reflects the greater absorption coefficient of the PBZT component.<sup>29</sup> The spectral sensitivity of a 50% BBL:PBZT blend photoreceptor (80-nm thick CGL), characterized by the ratio of initial photodischarge rate to incident light intensity which is proportional to the charge photogeneration quantum efficiency (see equation (1)), is also shown in Figure 7. The spectral response of charge photogeneration tracks the absorption spectrum very well (Figure 7), demonstrating that the blends of conjugated polymers provide a facile means of tuning the spectral sensitivity of organic photoelectronic devices.

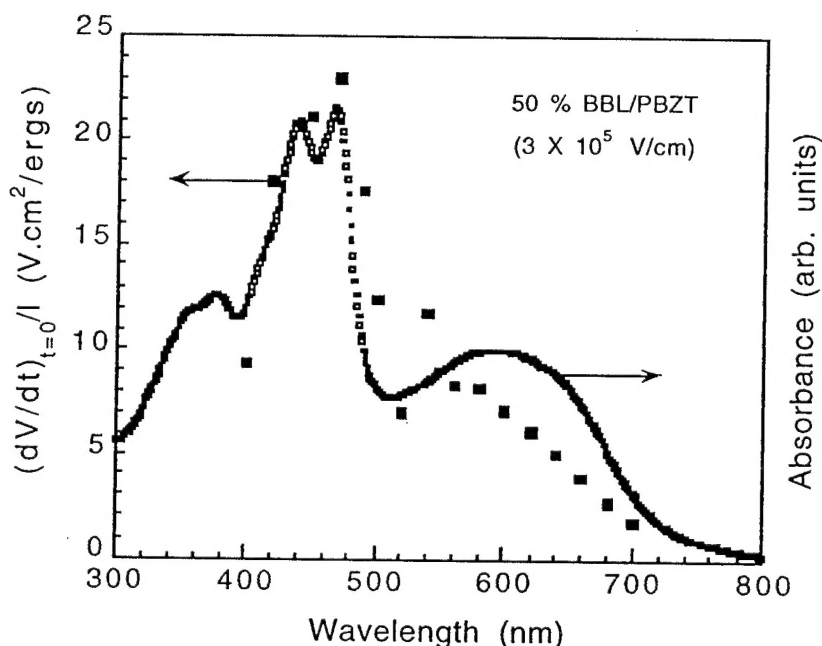


Figure 7. Spectral response of charge photogeneration in a 50-mol% BBL:PBZT blend photoreceptor and the blend absorption spectrum.

Figure 8 shows the field-dependent charge photogeneration quantum efficiency  $\phi(E)$  of a 50-nm thick BBL:PBZT (10 mol% BBL)/TTA photoreceptor along with similar data for the pure homopolymer photoreceptors (20-nm thick PBZT and 20-nm thick BBL). In spite of the possible size effects favoring the homopolymer-based photoreceptors with thinner CGL, the 10% blend photoreceptor has quantum yield  $\phi(E)$  that is comparable to the pure PBZT device at electric fields below  $10^5$  V/cm. At higher fields ( $>10^5$  V/cm), the 10% blend has superior carrier photogeneration yields. At  $5 \times 10^5$  V/cm, for example, the 10% blend photoreceptor has a 45% quantum efficiency compared to 32% for the pure PBZT device and only 18% for the pure BBL device. This represents factors of 1.41 and 2.50 enhancements of charge photogeneration in the polymer blend device compared to those of the two homopolymer devices. Although the detail mechanism of this enhancement of charge photogeneration in conjugated polymer blend photoreceptors is yet to be established, it is likely related to the observed photoinduced electron transfer in such blends<sup>29</sup> which may increase the effective exciton diffusion length in the charge generation layer.

## CONCLUSIONS

Xerographic photoreceptors made from conjugated polymer thin film charge generation layers have been found to exhibit low dark decay, good photosensitivity over a wide spectral range in the visible, and high photocarrier generation efficiency which are comparable or superior to current organic photoreceptors. In addition, the excellent thermal stability and mechanical properties of conjugated polymer thin films and the relative ease of fabricating bilayer photoreceptors from them suggest that they are very promising for electrophotographic imaging and related optoelectronic applications. The observed nanoscale size effects on the performance of bilayer photoreceptors is related to both the *extrinsic* nature of charge photogeneration in the devices and the small exciton diffusion lengths in conjugated polymers. Thus the photocarrier generation efficiency of bilayer organic photoreceptors can be significantly enhanced if the CGL thickness is reduced to the nanoscale range and is comparable to the exciton diffusion length. The results of our study of charge photogeneration in binary blends of conjugated polymers show that they exhibit enhanced photocarrier generation efficiency as well as enhanced spectral range of photosensitivity compared to the component homopolymers.

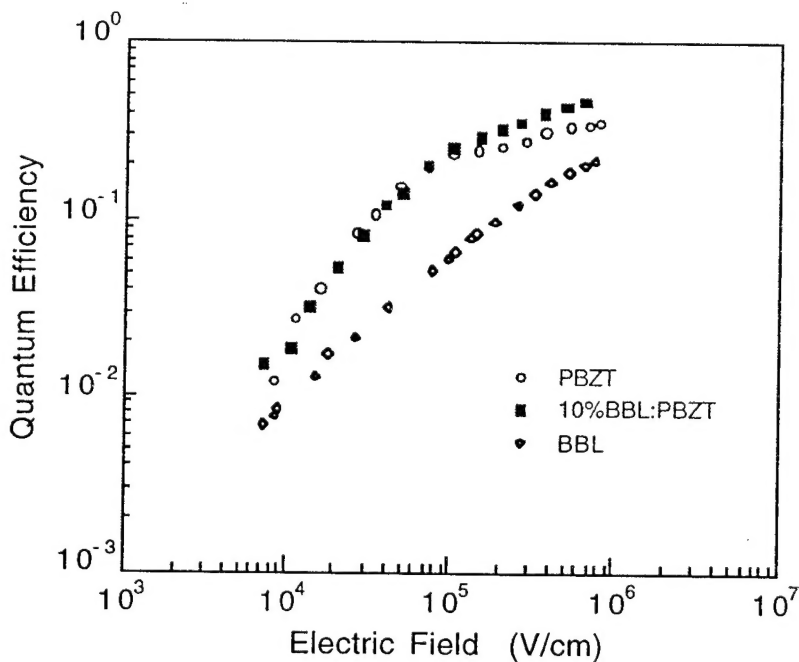


Figure 8. Charge photogeneration quantum efficiency dependence on electric field: BBL/TTA (20-nm BBL, 565-nm illumination); PBZT/TTA (20-nm PBZT, 470-nm illumination); and 10, mol% BBL:PBZT blend/TTA (50-nm thick, 470-nm illumination).

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